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EFFECT OF TALC STONE AND CHLORITE-TREMOLITE ROCK ON CERAMIC TILE PHASE COMPOSITION AND PROPERTIES

V. P. Il'ina^{1,2} and G. A. Lebedeva¹

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The following processes occur in talc stone (carbonate-chlorite-talc composition) and accompanying tremolite-chlorite rocks, studied in the present work, in the temperature interval 950 – 1100°C as a result of the decomposition of talc and tremolite: dehydration (talc, tremolite, chlorite), decarbonization (dolomite, calcite, breunnerite), and formation of new crystalline phases (forsterite, enstatite, clinoenstatite, subcalcium augite). These processes, as well as the presence of an amorphous phase enriched with magnesium ions, make ceramics stronger. Larger-size little-changed grains of tremolite are an additional strength-increasing factor. Owing to their tablet and needle shapes such grains reinforce the ceramic structure.

Key words: talc stone, tremolite-chlorite composition, clay, kilning, crystalline phases, glass phase.

Talc stone is a rock containing talc together with other minerals (calcium and magnesium carbonates, chlorite, tremolite). Talc with admixtures of these minerals is used abroad to improve the properties of ceramics. Talc with chlorite admixtures is used to increase the strength of ceramics (France, Austria, Italy); talc with magnesite (Canada, Finland) improves sintering, while talc with carbonate and tremolite admixtures decreases the deformation of articles during kilning (Sweden, USA). Moderate additions of talc to ceramic mixes used for domestically produced facing tiles make articles more heat-resistant [1].

Talc-bearing rocks containing chlorite, carbonate, and tremolite are common in the Republic of Karelia. There are two known deposits and 14 shows of talc stone. About half of them are located in the region of Lake Segozero (so-called Segozerskaya group) [2], and there are four known shows near the town of Kostomuksha. Talc stone belongs to a group of ultrabasic rocks with dunite-peridotite and peridotite-picrite composition that is common in the green-rock belts of the Karelian shield.

A talc stone body consists predominately of rocks with carbonate-chlorite-talc and carbonate-tremolite-chlorite composition with subordinate development of tremolite-chlorite varieties. Tremolite-chlorite rocks form small (2 to 20 m thick) lenticular and bed-like bodies in the talc-bearing rock mass.

The possibility of using talc stone as heat-shielding blocks for manufacturing fireplaces and household objects has been investigated [2, 3]. In the production of blocks, at least 50% of the waste material will consist of fine fractions of the rock mass (talc stone and accompanying rocks), requiring recovery. Fine fractions could be of interest as a corrective addition in ceramic tile mix.

To study the effect of the principal varieties of talc stone and accompanying chlorite-tremolite varieties on the properties of ceramic tile, samples were obtained from sections of the Turgan-Koivan-Allusta, Kalievo-Murnenanvaara, and Ozerki-1 deposits and from a large lenticular formation in the Kostomuksha shield.

The chemical composition of the rocks studied is presented in Table 1 and the mineral composition in Table 2. The mineral composition of the rocks was determined by optical microscopy and x-ray phase analysis and with a VEGA 2 LSH electron microscope with an attachment for performing microanalysis with magnification equal to $\times 150 - 1200$ (most often) and $\times 2000 - 4000$ (less often).

Microanalysis established that dolomite is the main carbonate minerals present in the rocks. But, in addition, negligible quantities of calcite and breunnerite are present in sample 1 (Table 2). Ore minerals consist mainly of magnetite (chromo-magnetite) and ilmenite. These samples differ by the quantitative content of the principal minerals and only negligibly by the chemical composition.

To determine the influence of the mineral composition of talc rocks on the properties and structure of ceramics,

¹ Institution of the Russian Academy of Sciences, Institute of Geology of the Karelia Scientific Center of the Russian Academy of Sciences (IG KarNTs RAN), Petrozavodsk, Republic of Karelia.

² E-mail: ivp@krc.karelia.ru.

TABLE 1. Chemical Compositions of Specimens of Talc Stone and Chlorite-Tremolite Rocks

Specimen No.	Sampling site, depth	Content, wt. %												
		SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	CO ₂	other
1	Section OZ-008 of Ozerki-1 (depth 11.25 m)	39.43	0.25	4.37	2.45	5.63	0.13	26.40	6.37	0.02	0.01	0.12	9.7	14.50
2	Turgan-Koivan-Allusta (Segozero), sample 53	36.40	0.22	4.59	6.82	3.76	0.20	26.57	5.63	0.02	—	0.02	—	15.40
3	Section OZ-010 of Ozerki-1 (depth 37.2 – 37.39 m)	39.06	0.55	8.29	5.25	9.34	0.14	24.50	4.39	0.18	0.01	0.49	—	7.50
4	Kalieva-Murenanvaara (Segozero), sample 506	50.38	0.16	4.89	1.77	7.61	0.33	21.57	9.63	0.11	0.02	0.21	—	2.84
5	Kostomukshskoe, sample A	40.01	0.36	6.07	0.69	8.26	0.14	26.20	4.77	0.02	0.07	0.08	—	12.90
6	Ivinskoe clay (Ladvinskii section)	61.44	0.85	17.12	4.25	1.18	0.09	2.44	1.23	1.82	3.01	—	—	6.01

TABLE 2. Mineral Composition of Specimens

Specimen No.*	Mineral variety	Content, wt. %				
		Carbonates	Chlorite	Tremolite	Talc	Ore
1	Talc stone (carbonate-chlorite-talc)	21	33	—	42	4
2	Chlorite-talc-carbonate	20	40	—	35	5
3	Tremolite-chlorite	< 1	55	33	5	7
4	Chlorite-tremolite	—	28	70	—	2
5	Chlorite-talc-carbonate-tremolite	15	38	5	35	—

* Sampling site, depths are presented in Table 1.

two-component ceramic mixes containing 30%³ talc rock and 70% local polymineral clay from the Ivinskoe deposit (Ladvinskii section) were investigated. The chemical composition of the clay is presented in Table 1 (specimen 6). The principal constituents of the clay are hydromica, quartz, feldspars (albite — oligoclase, potassium feldspar) and secondary minerals. The secondary minerals are chlorite and amphibole.

The amount of flux (30%) in ceramic mix was established previously as optimal for good sintering of the mixes based on Cambrian clay from the Chekalovskoe deposit and talc rocks from Segozero [4].

Conventional technology was used to investigate the mixes.

Mix preparation included the following: drying, comminution, sieving, weighing, and mixing the components in a laboratory ball mill to residue 0.063 – 1.5% on the sieve. The working moisture content of the mixes was 18 – 20% after standing for one day. Tiles with the dimensions 50 × 50 × 8 mm were formed from the mixes. The tiles were

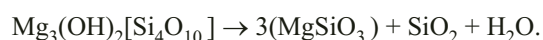
pre-dried at 105°C and kilned in a laboratory silit furnace at 950 and 1100°C (in accordance with the kilning temperature used in the ceramic brick manufacture 950°C and facing tile 1100°C in manufacture). The temperature was increased at the average rate 2 – 3 K/min, and the soaking time of the samples in the furnace at the required temperature was 40 min. The samples were allowed to cool down together with the furnace.

During kilning (to 1100°C) the minerals present in talc stone — talc, calcium magnesium, carbonates, chlorite, and tremolite — undergo phase transformations with new crystalline phases being formed.

Dehydration with release of water from the brucite and tetrahedral layers and chlorite recrystallization are observed in the range 480 – 800°C [5, 6].

Carbonates (calcite, dolomite, magnesite, breunnerite) dissociate in the temperature interval 600 – 800°C with CO₂ loss. Calcium and magnesium oxides form on decomposition [5].

Talc undergoes dehydration at 960°C and under further heating enstatite and cristobalite form in the reaction [7]



Water of crystallization is removed from tremolite $\text{Ca}_2\text{Mg}_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$ at 930 – 980°C with destruction of the amphibole structure and formation of cristobalite and pyroxene (augite) of the diopside-clinoenstatite series via the reaction [7]



X-ray phase analysis was performed on samples 1 (talc stone) and 3 (tremolite-chlorite rock), which were heat-treated at 1100°C, using an ARL X'TRA diffractometer with CuK1 radiation at angles $2\theta = 2 - 90^\circ$ and the Siroquant computer program.

It was established that the crystalline phases appearing when talc stone (specimen 1) is heated to 1100°C are mine-

³ Here and below, content by weight.

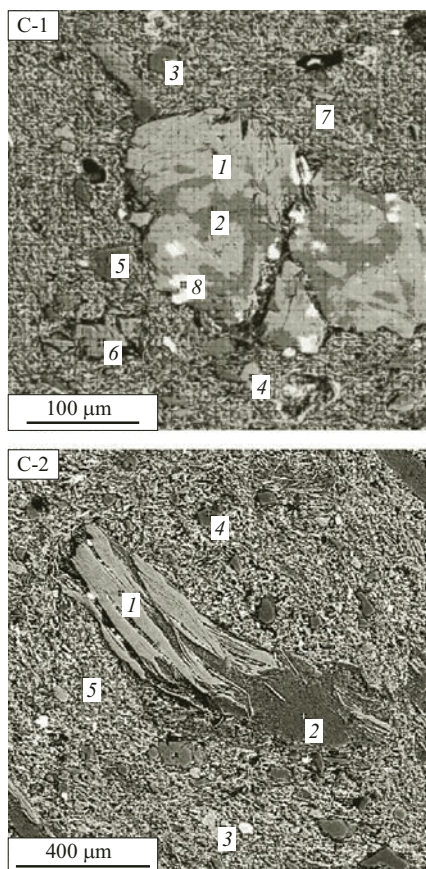


Fig. 1. Microstructure of ceramics C-1 and C-2 after firing at 950°C: C-1) added with talc stone [1) chlorite; 2) talc; 3) K-feldspar; 4) albite]; C-2) added with chlorite-tremolite [1) tremolite; 2) talc; 3, 5) albite; 4) K-feldspar; 6) chlorite; 7) fine binder; 8) magnetite].

erals in the pyroxene group (enstatite, protoenstatite, clinoenstatite). In addition, forsterite Mg_2SiO_4 , periclase MgO , and monticellite — orthosilicate $CaMg(SiO_4)$ are present. XPA data show that the glass phase amounts to 18.1% in specimen 1. On heating the tremolite-chlorite specimen 3 to 1100°C enstatite, clinoenstatite, hematite, and augite crystallize. XPA data show that the glass phase amounts to 19.4%.

Evidently, the minerals of the enstatite and forsterite group are products of crystallization of talc and chlorite. Periclase appears on dissociation of dolomite, while monticellite appears as a result of a reaction between CaO , MgO , and cristobalite, which form on decomposition of dolomite and talc while augite forms as a result of the recrystallization of tremolite.

According to electron microscopy data (Figs. 1 and 2) the ceramic tile samples possess a nonuniformly granular structure and consist of a binder consisting of fine grains ($< 10 \mu m$ in size) as well as larger grains, which range in size from 10 to 300 μm and are little-changed from those in the initial raw materials, disseminated in it. The large grains in ceramics consist of quartz, feldspars, talc, altered chlorite, tremolite, and ore minerals. The tremolite grains have

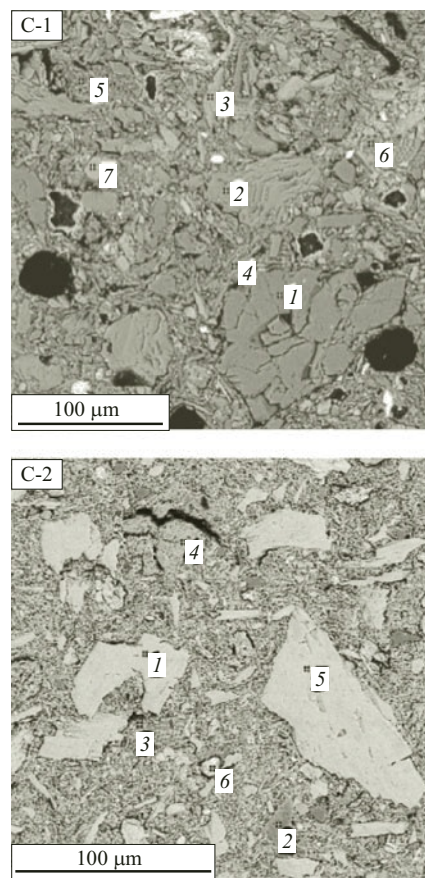


Fig. 2. Structure of ceramics C-1 and C-2 after firing at 1100°C: C-1) added with talc stone [1) quartz; 2) talc; 3, 4, 5, 6) amorphous phase; 4) K-feldspar]; C-2) added with chlorite-tremolite [1, 5) tremolite; 2) albite; 3, 4, 6) amorphous phase].

facetted and needle shapes. It is likely that after kilning the decomposition of minerals (chlorite, talc, tremolite, magnetite), established by DTA and RPA, in ceramics are associated to fine ($< 0.001 \text{ mm}$) fractions, while the large grains of these minerals remain little-changed.

According to electron microscopy, the principal binder (glass phase) has a complex aluminosilicate composition (%): 46.4 – 57.5 SiO_2 ; 0.5 – 1.36 TiO_2 ; 18.0 – 18.1 Al_2O_3 ; 5.2 – 7.4 $FeO + Fe_2O_3$; 1.2 – 1.9 CaO ; 4.3 – 7.4 MgO ; 1.2 – 2.0 Na_2O ; and, 2.3 – 3.5 K_2O . Compared with the composition of the initial clay the binder contains more MgO and less SiO_2 because the products of decomposition of magnesia silicates are present.

The properties of the ceramic samples (ceramic tiles) are presented in Table 3. The addition of talc stone as well as chlorite-tremolite rock as filler to low-melting hydromica clay increases the water absorption of ceramic tile by 2 – 3%, probably because of dehydration of carbonates and chlorites to 900°C. However, the water-absorption indicators do not exceed GOST 6141–91 requirements (no more than 16%). The strongest tiles are those containing additions of rock with high tremolite content (3, 4) during kilning at 950°C and at 1100°C.

TABLE 3. Properties of Ceramic Tiles with Additions of Talc Stone and Chlorite-Tremolite Rocks

Ceramic sample	Sample composition, wt.%		Post-kilning properties of ceramic samples					
	Ladivinskii clay*	Addition*	Kilning at 950°C			Kilning at 1100°C		
			Bending strength, MPa	Shrinkage, %	Water absorption, %	Bending strength, MPa	Shrinkage, %	Water absorption, %
C-1	70	30 (No. 1)	23.69	9.89	16.00	37.85	8.64	13.26
C-2	70	30 (No. 2)	25.66	10.20	13.25	35.43	8.20	12.76
C-3	70	30 (No. 3)	26.90	10.13	15.81	39.68	8.03	13.79
C-4	70	30 (No. 4)	27.18	9.45	14.67	42.94	8.87	12.99
C-5	70	30 (No. 5)	23.69	10.56	15.30	35.25	8.53	12.85
C-0	100	—	18.44	11.80	13.81	27.42	12.99	9.91

* See Tables 1 and 2, respectively, for the chemical and mineralogical compositions of mineral rock samples.

It can be supposed on the basis of the data obtained in this study that decomposition and recrystallization of chlorite, talc, and tremolite lattices with formation of fine crystal phases, a substantial fraction of which consists of pyroxene-group minerals, as well as the formation of a magnesium-enriched glassy (amorphous) phase as a result of the interaction of iron-magnesia minerals with clay minerals increase the strength of ceramic tile with additions of talc stone and chlorite-tremolite rocks. The high strength of ceramics containing pyroxene has also been noted in [8, 9]. The positive effect of pyroxenes on ceramic strength is explained by their reinforcing properties resulting from the non-isometric shape of the crystals. The larger grains of tremolite, which have plate and needle shapes, change little during kilning, and reinforce the ceramic mix in the kilning temperature range 950–1100°C, affect the increase of strength of ceramic with addition of a specimen with chlorite-tremolite composition. Ceramics with the fillers indicated are 1.5 times stronger after kilning at 1100°C compared with the previously obtained ceramic containing added feldspar raw materials (23–31 MPa) [10].

As a result of the present study of the effect of additions of talc stone and accompanying chlorite-tremolite rocks from Karelia on the properties of ceramic tile based on low-melting hydromica clay from the Ivinskoe deposit has established that these rocks hold promise as raw material for manufacturing strong ceramic tile. The use of wastes for this purpose from the production of block rock can solve the problem of their recovery.

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